# Low *trans*-isomers formation in the aqueous-phase Pt/TPPTS-catalyzed partial hydrogenation of methyl esters of linseed oil

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## A B S T R A C T

Very low formation of both undesired products namely *trans*-C18:1 esters and the fully saturated methyl stearate (MS) with high catalytic activities (TOF = 6820 h$^{-1}$) under mild reaction conditions have been achieved by water-dispersible platinum(0) nanoparticle catalysts stabilized by TPPTS ligands and the zwitterionic phospholipid surfactant lecithin in the partial hydrogenation of polyunsaturated methyl esters of linseed oil (MELO) into their monounsaturated counterparts in aqueous/organic micellar reactors. The reaction rate was independent of the stirring rate ensuring that mass transfer was not rate determining. The apparent activation energy of the Pt/TPPTS catalyst was calculated and amounts a low value of 17.8 kJ/mol. Employing Pt/TPPTS catalysts the starting material MELO possessing an iodine value (IV) of 202 was reduced to IV = 85 and contained only 2.4 mol% of *trans*-C18:1 esters. In contrast, in the traditional industrial partial hydrogenation process of soybean oil possessing an IV of 130 reduced over commercial Ni-based catalyst to IV = 80 the *trans*-fats content was ∼30 mol% whereas with a further reduction to IV = 70 to produce all-purpose shortenings the *trans*-fats level reached a higher value of ∼45 mol%. In the aqueous-phase catalysis, in the range of 55–70 IVs for the hydrogenated products of MELO the Pt/TPPTS catalysts gave the least amount of *trans*-C18:1 esters followed by Rh/TPPTS and then by Pd/TPPTS complexes. Interestingly, with Pt/TPPTS catalysts the formation of MS was very low compared with Pd/TPPTS and Rh/TPPTS systems. Over highly active heterogeneous Pt/Al$_2$O$_3$ (5 wt.%) catalysts the formation of *trans*-C18:1 esters was low whereas the content of MS was high (37.7 mol%) compared with the very low formation of MS (2.93 mol%) with Pt/TPPTS catalysts. Even at a reduction level of IV = 72 a sufficient amount of C18:3 esters (2.9 mol%) still remained over Pt/Al$_2$O$_3$ catalysts whereas with Pt/TPPTS at IV = 70 the conversion of C18:3 esters was quantitative. A recycling experiment at a higher temperature of 80 °C showed that the catalytic activity of water-dispersible platinum(0) nanoparticle catalysts stabilized by TPPTS remained high in a consecutive run and possess the potential to be recycled without any loss of catalytic activity. This partial hydrogenation reaction of MELO employing platinum(0) nanoparticle-TPPTS-lecithin-stabilized catalytic systems is an interesting model of a catalytic reaction for studying the selective partial hydrogenation of edible vegetable oils to foodstuffs with very low or zero amounts of both undesired products namely *trans*-fats and fully saturated fats employing environmentally attractive aqueous/organic two-phase systems.

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## 1. Introduction

The partial hydrogenation of edible vegetable oils constituted a major industrial process to modify oils and fats in terms of increased oxidative stability to prolong the shelf life of the product combined with improved physical properties such as higher melting points and solid fat contents in order to provide the required mouth feel, texture and other characteristics of the food. Heterogeneous catalytic systems based on nickel were the choice of the edible oils hydrogenation processing industry which has a long history started in 1902 with the first patent filed by Wilhelm Normann to the Leprince [1]. This patent was filed five years after the great discovery

of P. Sabatier and J. B. Senderens in 1897 of the gas phase hydrogenation reaction of ethylene to ethane catalyzed by finely divided nickel and because of the great importance of this novel reaction applicable not only on olefins but also on a broad spectrum of different organic and inorganic starting materials such as aromatics *e.g.* benzene, ketones, aldehydes, nitriles, carbon monoxide etc., which actually paved the way for the development of numerous catalytic industrial processes, in 1912 P. Sabatier was awarded the Nobel Prize in Chemistry [2,3]. Based on the patent filed by Wilhelm Normann the British firm Joseph Crosfield & Sons developed in 1906 the industrial hydrogenation process using as feedstock whale oil and the first commercial plant of Procter & Gamble went on stream in 1911 with the appearance of the first industrially produced shortening named "Crisco" obtained by hydrogenation of cottonseed oil feedstocks [4–8].

The catalytic partial hydrogenation of edible oils especially of soybean oil became in the period 1950 – 1980 the main activity in the vegetable oil processing industry. Current cardiovascular guidelines encourage low consumption of saturated fats based on results of studies in the 1950s which showed that there is a direct association between consumption of saturated fats and cardiovascular disease (CVD). It should be mentioned, however, that a recent investigation [9] based on 76 studies with 659 300 participants (27 of these studies are randomized controlled trials possessing a higher strength of evidence with 103 000 participants) has not clearly provided supportive evidence for current cardiovascular guidelines that encourage low consumption of saturated fats. In the past, the industrial Ni-catalyzed partial hydrogenation process of edible oils so-called "fat hardening process" produced up to 50% *trans*-fats formed via *cis/trans* isomerization side-reactions [10,11]. In the 1990s, *trans*-fats have raised serious health concerns from reports that they are considered to be strongly correlated with a higher concentration of plasma LDL-cholesterol and consumption of *trans*-fats provides no apparent nutritional benefit and possesses a considerable potential for harm [12–28]. On a gram-for-gram basis, consumption of *trans*-fats possesses an about 15 times greater risk of CVD than of saturated fats [29]. Based on these reports and findings many countries have changed their regulations in order to protect the people regarding the consumption of *trans*-fats [12–29]. For example, regulations were introduced in Denmark by January 2004 to restrict the use of industrially produced *trans*-fats in edible fats to 2 wt% in any food product making possible that people consume <1 g industrially produced *trans*-fats per day. Such regulations were also introduced by other countries *e.g.* Switzerland. However, other countries *e.g.* USA have made decisions of labeling the *trans*-fats content on the nutrition facts panel of foods and such a decision was introduced by the Food and Drug Administration (FDA) by 1 January 2006. Very recently, FDA has banned the use of *trans*-fats in foods giving to the food manufactures and foodservice establishments a period of 3 years to reformulate their food products [30]. All these regulations have caused a demand for foodstuffs products with lower or zero amounts of *trans*-isomers content [12–30].

Therefore, there have been numerous studies for the development of novel highly selective catalysts for the partial hydrogenation of edible oils producing very low amounts or preferably zero amounts of *trans*-fats. For example, the group of Jacobs [7,31–33] demonstrated that shape-selective hydrogenation of edible oils catalyzed by Pt clusters encapsulated in the pores of ZSM-5 zeolites results in a significant reduction of *trans*-fats in the hardened product containing low amounts of trisaturated triglycerides. Cheng et al. [34] partially hydrogenated soybean and cottonseed oil triglycerides using commercial heterogeneous Ni-based Nysosel 820, Pt/C (5 wt.%) and Pd/C (5 wt.%) catalysts and found that the Pt-based catalyst yielded the least amount of *trans*-fats followed by Ni and then by Pd for both oil triglycerides in the range of IV

(Iodine Values) 70–95 for the hardened product with, however, noticeable less *trans*-fats to be formed with cottonseed oil than the soybean oil feedstock probably because cottonseed oil contains lower amounts of C═C units. Iida et al. [35] investigated the effect of various supports on the activity and selectivity of Pt-based heterogeneous catalysts for the partial hydrogenation of soybean oil at IV 70 and found that $Pt/BaSO_4$ was the most effective catalyst to obtain low levels of both *trans*-fats and additional saturated fats. McArdle et al. [36] reported various supported platinum and palladium catalysts compared with conventional nickel catalysts applied in the selective hydrogenation of sunflower oil and showed that the Pt-based catalyst was the most effective in reducing the *trans*-fats formation. Numwong et al. [37] studied the partial hydrogenation of methyl esters of rapeseed oil using heterogeneous Pt, Pd and Ni catalysts and found that Pt-based catalysts exhibited the lowest selectivity towards *trans*-C18:1 fatty esters with the highest formation of the saturated methyl stearate which could be probably explained due to the high catalytic activity of Pt-based catalyst to hydrogenate *trans*-C18:1 isomers into the C18:0 methyl stearate end product.

Catalysis by water-soluble transition metal complexes in aqueous/organic two-phase systems attracts an enormous interest because this mode of heterogenization of homogeneous catalysis combines several advantages such as: (i) high activities and selectivities under mild reaction conditions by tailoring of the coordination sphere of the metal, (ii) easy and quantitative recovery of the catalyst in active form from organic reaction products by simple phase separation and easy catalyst recycling. Therefore, numerous steps in conventional industrial processes are rendered superfluous and process engineering is enormously simplified resulting in substantial energy savings and lower emissions, (iii) novel types of catalytic reactivity have been observed in water in several different kinds of catalytic reactions, (iv) the large heat capacity of water makes it an excellent medium to perform exothermic reactions such as hydrogenation reactions more safer and more selective which is especially important in large scale exothermic catalytic processes and (v) water is non-toxic, non-inflammable, odourless and colourless for easy detection of impurities, *i.e.* it is a green solvent that can replace conventional, environmentally less desirable solvents, and it is inexpensive and abundantly available [38–43]. Water-soluble rhodium and ruthenium catalytic complexes modified with the sodium salt of trisulfonated triphenylphosphine [TPPTS, $P(C_6H_4$-$m$-$SO_3Na)_3$] have found important industrial applications such as in the biphasic Ruhrchemie/Rhône-Poulenc process for the hydroformylation of lower olefins i.e. propene and raffinate II mixture rich in 1-butene [raffinate II is a mixture of 1-butene, 2-butenes (*cis/trans*) and butanes (*n*-/iso) obtained from $C_4$-stream of naphtha crackers] and in the Rhône-Poulenc processes of the addition of active C—H compounds to dienes for the synthesis of vitamin E and A intermediates and the hydrogenation of α, β-unsaturated aldehydes to the corresponding allylic alcohols in aqueous/organic two-phase systems [39,40]. Our group [44–47] studied the biphasic partial hydrogenation of renewable polyunsaturated methyl esters of linseed, sunflower, soybean and *Cynara cardunculus* oils in order to achieve high selectivities up to 79.8 mol% of monounsaturated (C18:1) fatty acid methyl esters (FAME) which is biodiesel fuel of increased oxidative stability, energy and environmental performance at a low pour point catalyzed by water-soluble Rh/TPPTS and Ru/TPPTS complexes which, however, produced high amounts (up to 46.3 mol%) of *trans*-C18:1 fatty esters. Various water-soluble Pt/TPPTS complexes have been synthesized by several groups namely of Patin [48], Herrmann [49], Hirano [50] and Atwood [51–56]. However, only one study of a catalytic hydrogenation reaction has been reported so far which uses bimetallic water-soluble Ru/Pt-TPPTS catalysts for the selective biphasic hydrogenation of halonitroaromatic compounds [57].

**Table 1**
Effect of P/Pt molar ratio and reaction time on the Pt/TPPTS-catalyzed hydrogenation of MELO in aqueous/organic two-phase systems[a].

| Entry | Starting Material | Catalyst Precursor | P/Pt Molar ratio | t (min) | C18:3 (total) (mol%) | C18:2 (total) (mol%) | C18:1 (total) (mol%) | cis-C18:1 (mol%) | trans-C18:1 (mol%) | MS (mol%) | IV[b] | TOF[c] (h$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| – | MELO[d] | – | – | – | 59.3[e] | 16.9[f] | 20.5[g] | 20.5[g] | – | 3.3 | 202 | – |
| 1/1[h] | MELO | PtCl$_2$/TPPTS | 3 | 5 | 22.7 | 25.7 | 41.4 | 40.0 | 1.4 | 10.2 | 139 | 4400 |
| 1/2[h] | MELO | PtCl$_2$/TPPTS | 4 | 5 | 26.0 | 24.5 | 39.7 | 38.7 | 1.0 | 9.8 | 145 | 4000 |
| 1/3[h] | MELO | PtCl$_2$/TPPTS | 6 | 5 | 26.9 | 24.8 | 38.1 | 37.0 | 1.1 | 10.2 | 146 | 3900 |
| 1/4[h] | MELO | PtCl$_2$/TPPTS | 8 | 5 | 28.6 | 24.4 | 37.0 | 35.9 | 1.1 | 9.9 | 149 | 3700 |
| 1/5[h] | MELO | PtCl$_2$/TPPTS | 10 | 5 | 30.1 | 25.2 | 34.2 | 33.2 | 1.0 | 10.5 | 152 | 3500 |
| 1/6[i] | MELO | PtCl$_2$/TPPTS | 12 | 5 | 34.3 | 23.3 | 34.3 | 33.6 | 0.7 | 8.1 | 160 | 3000 |
| 1/7[i] | MELO | PtCl$_2$/TPPTS | 14 | 5 | 33.6 | 23.9 | 33.6 | 32.9 | 0.7 | 8.9 | 158 | 3000 |
| 1/8[j] | MELO | PtCl$_2$/TPPTS | 20 | 5 | 52.7 | 18.9 | 23.8 | 23.7 | 0.1 | 4.6 | 191 | 800 |
| 1/9[h] | MELO | PtCl$_2$/TPPTS | 12 | 10 | 13.9 | 35.0 | 39.2 | 37.7 | 1.5 | 11.9 | 131 | 2700 |
| 1/10[h] | MELO | PtCl$_2$/TPPTS | 12 | 20 | 2.6 | 18.5 | 54.1 | 51.7 | 2.4 | 24.8 | 85 | 1700 |
| 1/11[h] | MELO | PtCl$_2$/TPPTS | 12 | 30 | 0 | 6.8 | 50.7 | 46.6 | 4.1 | 42.5 | 55 | 1400 |
| 1/12[h] | MELO | PtCl$_2$/TPPTS | 12 | 60 | 0 | 2.5 | 42.9 | 38.2 | 4.7 | 54.6 | 41 | 730 |

[a]  Reaction conditions: T = 60 °C; P$_{H2}$ = 30 bar; 2.66 mg (0.01 mmol) PtCl$_2$, 1.6165 g (10.0 mmol of C=C units) of MELO mixture (C=C/Pt molar ratio = 1000); 10 ml deaerated demineralized water, [Pt] = 200 ppm, pH = 3.32–4.29. Addition of MELO mixture to the aqueous catalyst solution results a two-phase system with a volume ratio of aqueous/organic phase = 10/1.3; magnetic bar stirring (stirring rate = 700 rpm).

[b]  IV (Iodine Values) were calculated from the FAME levels from GC data through equation IV = 0.860 x (C18:1) + 1.732 x (C18:2) + 2.616 x (C18:3) according to the AOCS Official Method Cd 1c-85 [34].

[c]  Defined as mole of hydrogenated C=C units in the C18:3, C18:2, and C18:1 compounds in both the starting material MELO mixture and all other regiomers/stereoisomers formed during the course of the reaction per mole of platinum per hour.

[d]  MELO except of α-MLN, ML, MO and MS further contained 5.1% of methyl palmitate (MP, C16:0) which was ignored in the experiments.

[e]  Methyl α-linolenate (α-MLN), C18:3 (9c, 12c, 15c).

[f]  Methyl linoleate (ML), C18:2 (9c, 12c).

[g]  Methyl oleate (MO), C18:1 (9c).

[h]  Black precipitate presumed to be metallic platinum. At lower TPPTS/Pt molar ratios a larger amount of metallic platinum was observed.

[i]  Small amount of metallic platinum.

[j]  No metallic platinum formation.

We here report an investigation on the *trans*-isomers formation in the partial hydrogenation of methyl esters of linseed oil employing water-soluble Pt/TPPTS catalyst in aqueous/organic two-phase systems. To our knowledge, this is the first example of a catalytic hydrogenation reaction using Pt/TPPTS catalysts in aqueous media.

## 2. Experimental

### 2.1. Materials

Hydrogen (quality 5.0) was purchased from Air Liquide Hellas A.E.B.A. (Athens) and used without further purification. Demineralized water was deoxygenated in an ultrasound bath under high vacuum for 2 h. During the deoxygenation the flask was disconnected from the vacuum, and the aqueous solvent was saturated with argon; this procedure was repeated several times. PtCl$_2$, RhCl$_3$·3H$_2$O, RuCl$_3$·3H$_2$O and PdCl$_2$ were purchased from Alfa Aeser, Acros Organics, Alfa Aeser and Fluka, respectively, and were used without any further purification. TPPTS was prepared according to literature procedures [58–65] and isolated with purity higher than 98%. Linseed oil was purchased from MP Biomedicals and was used without any further purification.

### 2.2. Typical transesterification reaction of linseed oil with methanol

Typical transesterification reaction of linseed oil: A 1000-ml, three-necked, round-bottom flask, equipped with a mechanical stirrer, a thermometer and a condenser was charged with 283.0 g of linseed oil and a solution of 190.0 g methanol containing 2.99 g of NaOH. The mixture was stirred at 55–59 °C for 120 min. The course of the reaction was followed by thin layer chromatography. The reaction mixture was then cooled and further stirred for 60 min at room temperature. After phase separation resulted in the isolation of the methyl esters of linseed oil (MELO) and the glycerol. The glycerol phase (bottom layer) was removed and kept in a separate container. The MELO phase (top layer) was washed with distilled water several times (pH = 5.6), dried over Na$_2$SO$_4$ to obtain 211.68 g of crude MELO mixture which was used as starting material in the hydrogenation reaction without any purification by distillation. Methyl esters composition of linseed oil was determined by gas chromatography (vide infra) and is given for the product of the first transesterification reaction as MELO in Tables 1–3 and of the second transesterification reaction as MELO1 in Table 4.

### 2.3. Procedure of a typical catalytic hydrogenation experiment

First, the autoclave was thoroughly cleaned and followed by numerous series of treatment of the autoclave at elevated temperatures (120 °C) and pressures (50 bar of H$_2$) within 1 h each time in the presence of TPPTS/water in the absence of any transition metals in order to be sure that no memory effects of the autoclave regarding previous transition metal catalytic systems are still operative. After this procedure, the hydrogenation reactions of MELO, MELO1 and MELO2 were carried out in the presence of water-soluble transition metal TPPTS complexes in aqueous/organic two-phase systems. The biphasic catalytic hydrogenation experiment of MELO of entry 1/6 of Table 1 was carried out with the following procedure. The water-soluble Pt/TPPTS catalyst precursor was first synthesized by dissolving under stirring of 2.66 mg (0.01 mmol) PtCl$_2$ and 72.44 mg (0.12 mmol) TPPTS, (TPPTS/Rh molar ratio = 12) under argon in 10 ml deaerated demineralized water within 10 min of time. This aqueous Pt/TPPTS catalyst precursor solution, having a platinum concentration of 200 ppm, was charged into an *Autoclave Engineers* autoclave equipped with a glass liner of a nominal volume of 100 ml which was previously evacuated and filled with argon together with 1.6165 g (10.0 mmol C=C units) of MELO which results a two-phase system with a volume ratio of aqueous/organic phase = 10/1.3. In this biphasic reaction mixture the molar ratio of C=C units/Pt was 1000. After a number of pressurising-depressurising cycles with hydrogen to remove last traces of air oxygen, the autoclave was pressured and contents were heated with stirring using a stir bar driven by an IKA magnetic stirrer (poorer mixing) because its own MagneDrive III agitator system

**Table 2**
Effect of temperature on the Pt/TPPTS-catalyzed hydrogenation of MELO in aqueous/organic two-phase systems[a].

| Entry | Starting Material | Catalyst Precursor | T (°C) | C18:3 (total) (mol%) | C18:2 (total) (mol%) | C18:1 (total) (mol%) | cis-C18:1 (mol%) | trans-C18:1 (mol%) | MS (mol%) | IV[b] | TOF[c] (h$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| – | MELO[d] | – | – | 59.3[e] | 16.9[f] | 20.5[g] | 20.5[g] | – | 3.3 | 202 | – |
| 2/1[h] | MELO | PtCl$_2$/TPPTS | 50 | 41.3 | 21.9 | 29.5 | 29.1 | 0.4 | 7.3 | 171 | 2160 |
| 2/2[h] | MELO | PtCl$_2$/TPPTS | 60 | 34.3 | 23.3 | 34.3 | 33.6 | 0.7 | 8.1 | 160 | 3000 |
| 2/3[h] | MELO | PtCl$_2$/TPPTS | 70 | 28.7 | 24.7 | 37.1 | 36.0 | 1.1 | 9.5 | 150 | 3670 |
| 2/4[h] | MELO | PtCl$_2$/TPPTS | 80 | 18.0 | 24.8 | 45.3 | 43.3 | 2.0 | 11.9 | 129 | 5000 |
| 2/5[h] | MELO | PtCl$_2$/TPPTS | 90 | 15.1 | 24.4 | 48.0 | 45.8 | 2.2 | 12.5 | 123 | 5300 |
| 2/6[h] | MELO | PtCl$_2$/TPPTS | 100 | 3.7 | 18.7 | 59.1 | 54.8 | 4.3 | 18.5 | 93 | 6670 |
| 2/7[h] | MELO | PtCl$_2$/TPPTS | 110 | 3.5 | 18.8 | 59.4 | 54.4 | 5.0 | 18.3 | 93 | 6700 |
| 2/8[h] | MELO | PtCl$_2$/TPPTS | 120 | 2.5 | 17.4 | 61.1 | 55.4 | 5.7 | 19.0 | 89 | 6820 |

[a] Reaction conditions: $P_{H2}$ = 30 bar; t = 5 min; 2.66 mg (0.01 mmol) PtCl$_2$, 72.44 mg (0.12 mmol) TPPTS (TPPTS/Pt molar ratio = 12); 1.6165 g (10.0 mmol of C=C units) of MELO mixture (C=C/Pt molar ratio = 1000); 10 ml deaerated demineralized water, [Pt] = 200 ppm, pH = 3.16–3.99. Addition of MELO mixture to the aqueous catalyst solution results a two-phase system with a volume ratio of aqueous/organic phase = 10/1.3; magnetic bar stirring (stirring rate = 700 rpm).

[b] IV (Iodine Values) were calculated from the FAME levels from GC data through equation IV = 0.860 x (C18:1) + 1.732 x (C18:2) + 2.616 x (C18:3) according to the AOCS Official Method Cd 1c-85 [34].

[c] Defined as mole of hydrogenated C=C units in the C18:3, C18:2, and C18:1 compounds in both the starting material MELO mixture and all other regiomers/stereoisomers formed during the course of the reaction per mole of platinum per hour.

[d] MELO except of α-MLN, ML, MO and MS further contained 5.1% of methyl palmitate (MP, C16:0) which was ignored in the experiments.

[e] Methyl α-linolenate (α-MLN), C18:3 (9c, 12c, 15c).

[f] Methyl linoleate (ML), C18:2 (9c, 12c).

[g] Methyl oleate (MO), C18:1 (9c).

[h] Black precipitate presumed to be metallic platinum.

**Table 3**
Effect of hydrogen pressure and C=C/Pt molar ratio on the Pt/TPPTS-catalyzed hydrogenation of MELO in aqueous/organic two-phase systems[a].

| Entry | Starting Material | Catalyst Precursor | $P_{H2}$ (bar) | C=C/Pt molar ratio | T (°C) | C18:3 (total) (mol%) | C18:2 (total) (mol%) | C18:1 (total) (mol%) | cis-C18:1 (mol%) | trans-C18:1 (mol%) | MS (mol%) | IV[b] | TOF[c] (h$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| – | MELO[d] | – | – | – | – | 59.3[e] | 16.9[f] | 20.5[g] | 20.5[g] | – | 3.3 | 202 | – |
| 3/1 | MELO | PtCl$_2$/TPPTS | 20 | 1000 | 60 | 39.7 | 22.1 | 31.4 | 30.9 | 0.5 | 6.8 | 169 | 2350 |
| 3/2[h] | MELO | PtCl$_2$/TPPTS | 30 | 1000 | 60 | 34.3 | 23.3 | 34.3 | 33.6 | 0.7 | 8.1 | 160 | 3000 |
| 3/3[h] | MELO | PtCl$_2$/TPPTS | 40 | 1000 | 60 | 28.7 | 24.3 | 36.9 | 35.9 | 1.0 | 10.1 | 149 | 3670 |
| 3/4[h] | MELO | PtCl$_2$/TPPTS | 50 | 1000 | 60 | 23.9 | 24.8 | 39.3 | 38.1 | 1.2 | 12.0 | 139 | 4250 |
| 3/5[h] | MELO | PtCl$_2$/TPPTS | 30 | 1000 | 80 | 0.2 | 7.5 | 56.9 | 50.2 | 6.7 | 35.4 | 62 | 2060 |
| 3/6[h] | MELO | PtCl$_2$/TPPTS | 30 | 2000 | 80 | 10.5 | 24.2 | 52.6 | 49.7 | 2.9 | 12.7 | 115 | 2930 |
| 3/7[h] | MELO | PtCl$_2$/TPPTS | 30 | 3000 | 80 | 23.5 | 23.9 | 44.1 | 42.3 | 1.8 | 8.5 | 141 | 3220 |
| 3/8[h] | MELO | PtCl$_2$/TPPTS | 30 | 4000 | 80 | 28.2 | 24.0 | 41.1 | 39.6 | 1.5 | 6.7 | 151 | 3730 |

[a] Reaction conditions: t = 5 min; except entries 3/5–3/8, t = 20 min; 2.66 mg (0.01 mmol) PtCl$_2$, 72.44 mg (0.12 mmol) TPPTS (TPPTS/Pt molar ratio = 12); 10 ml deaerated demineralized water, [Pt] = 200 ppm, pH = 3.25–4.09. Addition of 1.6165 g (10.0 mmol of C=C units) of MELO mixture (C=C/Pt molar ratio = 1000) to the aqueous catalyst solution results a two-phase system with a volume ratio of aqueous/organic phase = 10/1.3; magnetic bar stirring (stirring rate = 700 rpm).

[b] IV (Iodine Values) were calculated from the FAME levels from GC data through equation IV = 0.860 x (C18:1) + 1.732 x (C18:2) + 2.616 x (C18:3) according to the AOCS Official Method Cd 1c-85 [34].

[c] Defined as mole of hydrogenated C=C units in the C18:3, C18:2, and C18:1 compounds in both the starting material MELO mixture and all other regiomers/stereoisomers formed during the course of the reaction per mole of platinum per hour.

[d] MELO except of α-MLN, ML, MO and MS further contained 5.1% of methyl palmitate (MP, C16:0) which was ignored in the experiments.

[e] Methyl α-linolenate (α-MLN), C18:3 (9c, 12c, 15c).

[f] Methyl linoleate (ML), C18:2 (9c, 12c).

[g] Methyl oleate (MO), C18:1 (9c).

[h] Black precipitate presumed to be metallic platinum.

was out of order (stirring rate = 700 rpm). At the reaction temperature of 60 °C the hydrogen pressure was 30 bar and the reaction time 5 min. After the reaction the autoclave was cooled to room temperature, vented of hydrogen and the biphasic reaction mixture removed. The upper organic layer was easily separated in a separatory funnel from the lower aqueous layer containing the catalyst and dried over sodium sulfate. The organic layer containing the product mixture was analyzed by gas chromatography (GC) after addition of methyl heptadecanoate as standard and the obtained results are given in entry 1/6 of Table 1. Emphasis has been placed in all reaction described in Tables 1–6 in order to obtain reproducible results.

### 2.4. Analysis of TPPTS, MELO and the products of the hydrogenation reactions

The purity of the TPPTS ligand was determined by quantitative $^{31}$P{$^1$H}NMR analysis in D$_2$O at 25 °C. δ TPPTS = −5.4 ppm.$^{31}$P{$^1$H}NMR spectra (121 MHz, referenced to external 85% H$_3$PO$_4$) were recorderd on a Varian Unity Plus 300/54 spectrometer. The various polyunsaturated, monounsaturated and saturated FAME isomers contained in the starting material MELO and the hydrogenation products were identified by comparison of GC and gas chromatography/mass spectrometry (GC/MS) analytic data with data for authentic samples. GC/MS was measured on a Varian Star 3400CX GC coupled with a Varian Saturn 2000 ion trap MS. The GC was equipped with a flame ionization detector (FID) and a SP-2560 capillary column (100 m × 0.25 mm i.d. × 0.2 μm film thickness) which was purchased from Supelco (Athens, Greece). The SP-2560 capillary column is one of the two columns applied in the approved American Oil Chemists' Society (AOCS) official method Ce 1h-05 for the determination of *cis*-, *trans*-, saturated, monounsaturated and polyunsaturated fatty acids in vegetable or non-ruminant animal oils and fats by capillary GLC method [66]. Carrier gas was He at 230 kPa. The oven temperature was initially at 170 °C for 0 min and then increased to 220 °C with a rate of 1 °C/min. The injector and detector temperatures were set at 220 °C and 230 °C, respectively. GC analyses were

**Table 4**
Effect of different transition metals modified with TPPTS and of heterogeneous $Pt/Al_2O_3$ system on the catalytic hydrogenation of MELO in aqueous/organic two-phase systems[a].

| Entry | Starting Material | Catalyst Precursor | C18:3 (total) (mol%) | C18:2 (total) (mol%) | C18:1 (total) (mol%) | cis-C18:1 (mol%) | trans-C18:1 (mol%) | MS (mol%) | IV[b] | TOF[c] (h$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|
| – | MELO1[d] | – | 54.9[e] | 16.9[f] | 24.3[g] | 24.3[g] | – | 3.9 | 194 | – |
| 4/1 | MELO1 | PdCl$_2$/TPPTS | – | 4.1 | 70.6 | 37.1 | 33.5 | 25.3 | 68 | 740 |
| 4/2 | MELO1 | RhCl$_3$·3H$_2$O/TPPTS | – | 3.3 | 57.4 | 29.2 | 28.2 | 39.3 | 55 | 750 |
| 4/3 | MELO1 | PtCl$_2$/TPPTS | – | 11.1 | 59.6 | 49.3 | 10.3 | 2.93 | 70 | 670 |
| | MELO2[d] | – | 56.8[e] | 17.0[f] | 22.5[g] | 22.5[g] | – | 3.7 | 197 | – |
| 4/4[h] | MELO2 | Pt/Al$_2$O$_3$ (5 wt.%) | 2.9 | 15.3 | 44.1 | 33.6 | 10.5 | 37.7 | 72 | 2200 |

[a] Reaction conditions: $T = 110\,°C$; $P_{H2} = 30\,bar$; $t = 60\,min$; 0.01 mmol transition metal chloride; 30.18 mg (0.05 mmol) TPPTS (TPPTS/Metal molar ratio = 5); 1.7133 g (10.0 mmol of C=C units) of MELO 1 mixture or 1.668 g (10.0 mmol of C=C units) of MELO2 (C=C/Metal molar ratio = 1000); 10 ml deaerated demineralized water; pH = 3.07–3.20 in entries 4/1–4/3 and pH = 4.89 in entry 4/4. Addition of MELO mixture to the aqueous catalyst solution results a two-phase system with a volume ratio of aqueous/organic phase = 10/1.3; magnetic bar stirring (stirring rate = 700 rpm).

[b] IV (Iodine Values) were calculated from the FAME levels from GC data through equation IV = 0.860 x (C18:1) + 1.732 x (C18:2) + 2.616 x (C18:3) according to the AOCS Official Method Cd 1c-85 [34].

[c] Defined as mole of hydrogenated C=C units in the C18:3, C18:2, and C18:1 compounds in both the starting material MELO mixture and all other regiomers/stereoisomers formed during the course of the reaction per mole of transition metal per hour.

[d] MELO1 and MELO2 except of α-MLN, ML, MO and MS further contained 5.1% of methyl palmitate (MP, C16:0) and 5.0% MP, respectively, which were ignored in the experiments.

[e] Methyl α-linolenate (α-MLN), C18:3 (9c, 12c, 15c).

[f] Methyl linoleate (ML), C18:2 (9c, 12c).

[g] Methyl oleate (MO), C18:1 (9c).

[h] $t = 15\,min$; 39.02 mg Pt/Al$_2$O$_3$ (5 wt.%) *i.e.* 1.96 mg (0.01 mmol) Pt.

**Table 5**
Recycling of Pt/TPPTS catalyst and the mercury poisoning test in the hydrogenation of MELO in aqueous/organic two-phase systems[a].

| Entry | Starting Material | Catalyst Precursor | P/Pt Molar ratio | C18:3 (total) (mol%) | C18:2 (total) (mol%) | C18:1 (total) (mol%) | cis-C18:1 (mol%) | trans-C18:1 (mol%) | MS (mol%) | IV[b] | TOF[c] (h$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| – | MELO2[d] | – | | 56.8[e] | 17.0[f] | 22.5[g] | 22.5[g] | – | 3.7 | 197 | – |
| 5/1 | MELO2 | PtCl$_2$/TPPTS | 18 | 14.0 | 22.5 | 42.7 | 37.9 | 4.8 | 20.8 | 112 | 1700 |
| 5/2[h] | MELO2 | Recycled catalyst | 18 | 22.1 | 22.4 | 37.3 | 33.8 | 3.5 | 18.2 | 129 | 1400 |
| 5/3 | MELO2 | PtCl$_2$/TPPTS | 16 | 16.7 | 22.2 | 39.6 | 35.6 | 4.0 | 21.5 | 116 | 1600 |
| 5/4[i] | MELO2 | PtCl$_2$/TPPTS/Hg | 16 | 53.3 | 17.3 | 23.6 | 23.4 | 0.2 | 5.8 | 190 | 140 |

[a] Reaction conditions: $T = 80\,°C$; $P_{H2} = 30\,bar$; $t = 30\,min$; 2.66 mg (0.01 mmol) PtCl$_2$; 111.3 mg (0.18 mmol) TPPTS (TPPTS/Pt molar ratio = 18) in entries 5/1 and 5/2; 95.7 mg (0.16 mmol) TPPTS (TPPTS/Pt molar ratio = 16) in entries 5/3 and 5/4; 3.331 g (20.0 mmol of C=C units) of MELO 2 mixture (C=C/Pt molar ratio = 2000); 10 ml deaerated demineralized water; [Pt] = 200 ppm, pH = 3.51–3.62. Addition of MELO mixture to the aqueous catalyst solution results a two-phase system with a volume ratio of aqueous/organic phase = 10/2.5; magnetic bar stirring (stirring rate = 700 rpm); after the reaction formation of a minor amount of metallic platinum.

[b] IV (Iodine Values) were calculated from the FAME levels from GC data through equation IV = 0.860 x (C18:1) + 1.732 x (C18:2) + 2.616 x (C18:3) according to the AOCS Official Method Cd 1c-85 [34].

[c] Defined as mole of hydrogenated C=C units in the C18:3, C18:2, and C18:1 compounds in both the starting material MELO mixture and all other regiomers/stereoisomers formed during the course of the reaction per mole of platinum per hour.

[d] MELO2 except of α-MLN, ML, MO and MS further contained 5.0% of methyl palmitate (MP, C16:0) which was ignored in the experiments.

[e] Methyl α-linolenate (α-MLN), C18:3 (9c, 12c, 15c).

[f] Methyl linoleate (ML), C18:2 (9c, 12c).

[g] Methyl oleate (MO), C18:1 (9c).

[h] The aqueous catalyst layer (10 ml) of entry 5/1, after separation of the upper organic phase, was re-used with addition of a new portion of 3.331 g (20.0 mmol of C=C units) of MELO2.

[i] Addition of 601.8 mg (3 mmol) Hg(0) which is an excess of 300 equiv. over the platinum catalyst.

**Table 6**
Effect of stirring rate on the Pt/TPPTS-catalyzed hydrogenation of MELO in aqueous/organic two-phase systems[a].

| Entry | Starting Material | Catalyst Precursor | Stirring rate (rpm) | C18:3 (total) (mol%) | C18:2 (total) (mol%) | C18:1 (total) (mol%) | cis-C18:1 (mol%) | trans-C18:1 (mol%) | MS (mol%) | IV[b] | TOF[c] (h$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| – | MELO2[d] | – | – | 56.8[e] | 17.0[f] | 22.5[g] | 22.5[g] | – | 3.7 | 197 | – |
| 6/1 | MELO2 | PtCl$_2$/TPPTS | 500 | 15.6 | 23.5 | 43.6 | 39.8 | 3.8 | 17.3 | 119 | 1600 |
| 6/2 | MELO2 | PtCl$_2$/TPPTS | 700 | 16.7 | 22.2 | 39.6 | 35.6 | 4.0 | 21.5 | 116 | 1600 |
| 6/3 | MELO2 | PtCl$_2$/TPPTS | 800 | 16.1 | 23.4 | 41.7 | 37.3 | 4.4 | 18.8 | 119 | 1600 |
| 6/4 | MELO2 | PtCl$_2$/TPPTS | 900 | 20.3 | 23.0 | 39.2 | 35.7 | 3.5 | 17.5 | 127 | 1500 |

[a] Reaction conditions: $T = 80\,°C$; $P_{H2} = 30\,bar$; $t = 30\,min$; 2.66 mg (0.01 mmol) PtCl$_2$, 95.7 mg (0.16 mmol) TPPTS (TPPTS/Pt molar ratio = 16); 3.331 g (20.0 mmol of C=C units) of MELO 2 mixture (C=C/Pt molar ratio = 2000); 10 ml deaerated demineralized water; [Pt] = 200 ppm, pH = 3.49–3.82. Addition of MELO mixture to the aqueous catalyst solution results a two-phase system with a volume ratio of aqueous/organic phase = 10/2.5; stir bar driven by an IKA magnetic stirrer (poorer mixing) because the own *Autoclave Engineers* MagneDrive III agitator system was out of order; after the reaction formation of a small amount of metallic platinum.

[b] IV (Iodine Values) were calculated from the FAME levels from GC data through equation IV = 0.860 x (C18:1) + 1.732 x (C18:2) + 2.616 x (C18:3) according to the AOCS Official Method Cd 1c-85 [34].

[c] Defined as mole of hydrogenated C=C units in the C18:3, C18:2, and C18:1 compounds in both the starting material MELO mixture and all other regiomers/stereoisomers formed during the course of the reaction per mole of platinum per hour.

[d] MELO2 except of α-MLN, ML, MO and MS further contained 5.0% of methyl palmitate (MP, C16:0) which was ignored in the experiments.

[e] Methyl α-linolenate (α-MLN), C18:3 (9c, 12c, 15c).

[f] Methyl linoleate (ML), C18:2 (9c, 12c).

[g] Methyl oleate (MO), C18:1 (9c).

performed on a Shimadzu GC–14 B equipped with a FID detector and a SP-2560 capillary column with conditions as described in the above mentioned GC/MS analyses.

## 3. Results and discussion

### 3.1. Selective partial hydrogenation of methyl esters of linseed oil (MELO) catalyzed by water-soluble Pt/TPPTS complexes in aqueous/organic two-phase systems

The aqueous-phase Pt/TPPTS-catalyzed partial hydrogenation reaction of polyunsaturated fatty acid methyl esters (FAME) selectively into their monounsaturated counterparts without or low formation of both *trans*-C18:1 isomers and the fully hydrogenated product i.e. methyl stearate (MS) is an interesting model of a catalytic reaction for studying the selective partial hydrogenation of edible vegetable oils to foodstuffs with zero amounts of undesired *trans*-fats and saturated fats employing environmentally attractive aqueous/organic two-phase systems. We chose the mixture of polyunsaturated methyl esters of linseed oil (MELO) because it mainly consists of α-MLN (Scheme 1, Tables 1–4) and constitutes a good model to investigate the whole spectrum of the selective partial Pt/TPPTS-catalyzed hydrogenation reaction: C18:3 → C18:2 → *cis*-C18:1 ⇸ C18:0 (Scheme 1).

#### 3.1.1. Effect of the TPPTS/Pt molar ratio

First, we investigated the influence of the P/Pt molar ratio on the partial hydrogenation of MELO catalyzed by water-soluble Pt/TPPTS complexes at a molar ratio of C=C units/Pt = 1000, a reaction temperature of 60 °C, 30 bar $H_2$ pressure and a platinum concentration of 200 ppm in water in the absence of any added organic solvent within 5 min of reaction time in aqueous/organic two-phase systems (Table 1, entries 1/1–1/8). As expected, the highest catalytic activity with a turnover frequency (TOF) of 4400 $h^{-1}$ was obtained at a low TPPTS/Pt molar ratio of 3 (entry 1/1) whereas at increasing ligand/metal molar ratios the catalytic activity decreases to give at a ratio of TPPTS/Pt = 20 a TOF value of only 800 $h^{-1}$ (entry 1/8). This lower catalytic activity at higher TPPTS/Pt molar ratios could probably be rationalized by assuming that a competition between the free TPPTS ligand and the C=C units of fatty esters for a coordination site on platinum takes place which may lead to a retardation in the activation of the MELO hydrogenation reaction. Similarly, Tóth et al. [67] have also observed a retarding effect of excess of water-soluble monosulfonated triphenylphosphine ligand [TPPMS, $PPh_2(C_6H_4$-$m$-$SO_3Na)$] added to ruthenium precursor in Ru/TPPMS-catalyzed hydrogenation reactions in aqueous media. The formation of undesired *trans*-C18:1 esters is strongly influenced by the amount of TPPTS added to the platinum precursor. At the low P/Pt molar ratio of 3 the formation of *trans*-C18:1 FAME was 1.4 mol% (entry 1/1) and at increasing TPPTS/Pt molar ratios the selectivity towards the *trans*-C18:1 isomers considerably decreases to give at a ratio of P/Pt = 20 only 0.1 mol% of *trans*-C18:1 esters (entry 1/8). The lower selectivity to *trans*-C18:1 esters at increasing TPPTS/Pt molar ratios could probably be explained with the competition between the free phosphine ligand and the carbon–carbon double bonds of the FAME mixture on the platinum coordination sphere which lowers the extent of the *cis/trans*-isomerization side reaction. After the hydrogenation reaction no metallic platinum formation was observed at the TPPTS/Pt molar ratio of 20 (entry 1/8) indicating no decomposition of the catalyst whereas at molar ratios TPPTS/Pt = 14 and 12 a small amount of metallic platinum was observed (entries 1/6, 1/7) and at molar ratios of TPPTS/Pt ≤ 10 larger amounts of metallic platinum were formed indicating decomposition of the catalyst (entries 1/1–1/5). The selectivity to the fully saturated product MS

depends on the amount of decomposed Pt/TPPTS catalyst to form metallic platinum and with increasing amount of metallic platinum formed in the mixture after the hydrogenation reaction increases the selectivity towards the product MS. For example, at the low P/Pt molar ratio of 3 where massive decomposition of the Pt/TPPTS catalyst was observed to form visible large amounts of metallic platinum the selectivity to MS was high namely 10.2 mol% (entry 1/1) whereas at the high molar ratio of P/Pt = 20 where no decomposition of the Pt/TPPTS catalyst and no formation of metallic platinum was observed the selectivity to MS was low i.e. 4.6 mol% (entry 1/8).

#### 3.1.2. Effect of reaction time

Table 1 (entries 1/6, 1/9–1/12) presents the activity and selectivity of the water-soluble Pt/TPPTS catalyst towards C18:1 FAME and MS as a function of reaction time in the hydrogenation reaction of MELO in aqueous/organic two-phase systems. The hydrogenation of MELO started immediately with hydrogen consumption without an induction period of the reaction. Therefore, no prereduction of the Pt/TPPTS catalyst was carried out and only made sure that the reaction conditions were well chosen in order to obtain reproducible results. All the following experiments were carried out systematically without a prior prereduction of the Pt/TPPTS catalyst. The selectivity towards *trans*-C18:1 esters and the fully saturated product MS increases with increasing reaction time from 5 up to 60 min to give selectivities to *trans*-C18:1 esters from 0.7 up to 4.7 mol% and to MS from 8.1 up to 54.6 mol% at a molar ratio of C=C units/Pt = 1000 and P/Pt = 12, a reaction temperature of 60 °C, 30 bar $H_2$ pressure and a platinum concentration of 200 ppm in aqueous/organic two-phase systems (Table 1, entries 1/6, 1/9–1/12). In the industrial "fat hardening" partial hydrogenation process of edible oils i.e. soybean oil with an iodine value (IV) of 130 reduced over commercial Ni-based catalyst to IV = 80 the *trans*-fats content was ~30% whereas with a further reduction to IV = 70 to produce all-purpose shortenings the *trans*-fats level reaches a higher value of ~45% [8]. In order to compare the amount of *trans*-fats produced in the Ni-catalyzed industrial hydrogenation process of edible vegetable oils with the amount of *trans*-C18:1 esters produced in the Pt/TPPTS-catalyzed partial hydrogenation of MELO (Tables 1–4) we calculated the IVs of the product mixtures in the Pt/TPPTS-catalyzed hydrogenation reaction from the FAME levels from the GC data through the following equation according to the AOCS Official Method Cd 1c-85 [34]: IV = 0.860 x (C18:1) + 1.732 x (C18:2) + 2.616 x (C18:3). The Pt/TPPTS catalytic system produced very low amounts of *trans*-C18:1 esters which are about ten times lower compared with the amounts of *trans*-fats formed with industrially applied nickel-based catalysts under comparable levels of reductions expressed in IVs. For example, in the presence of Pt/TPPTS catalysts the starting material mixture of MELO (IV = 202) reduced to IV = 85 contained only 2.4 mol% of *trans*-C18:1 esters (entry 1/10) whereas a further reduction to IV = 55 the content of *trans*-C18:1 esters remained low namely 4.1 mol% (entry 1/11). The selectivity to the total C18:1 esters increases with increasing reaction time to give within 5 min 34.3 mol% (entry 1/6) and in 20 min a total content of 54.1 mol% C18:1 esters (entry 1/10). At a longer reaction time of 60 min the selectivity to total C18:1 esters decreased to 42.9 mol% (entry 1/12). After the hydrogenation reaction with a duration of 5 min a small amount of metallic platinum was observed indicating a decomposition of the Pt/TPPTS catalyst to a smaller extent (entry 1/6) whereas at longer reaction times from 10 up to 60 min larger amounts of metallic platinum were formed at the end of the reaction (entries 1/9–1/12).

#### 3.1.3. Effect of temperature

The catalytic activity and selectivity towards C18:1 esters and MS in the Pt/TPPTS-catalyzed partial hydrogenation of MELO increases with increasing temperature from 50 °C up to 120 °C to
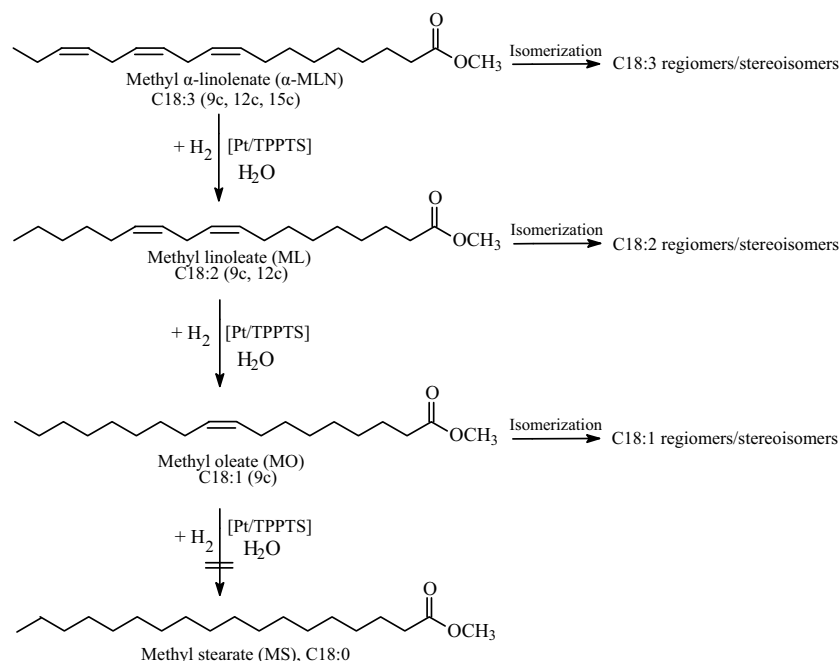
**Scheme 1.** Selective Pt/TPPTS-catalyzed hydrogenation of polyunsaturated methyl esters of linseed oil (MELO) into their *cis*-monounsaturated (C18:1) counterparts with low formation of *trans*-C18:1 isomers in aqueous/organic two-phase micellar systems. The term "regiomers/stereoisomers" refers to all region/stereo-isomers obtained from hydrogenation and/or positional isomerization (along the carbon chain) reactions and all other geometric isomers formed via *cis/trans* isomerization reactions.

give TOFs from 2160 up to 6820 $h^{-1}$ and selectivities to a total content of C18:1 ester regiomers/stereoisomers from 29.5 up to 61.1 mol% with MS formations of 7.3 up to 19.0 mol% at a molar ratio of C=C units/Pt = 1000 and P/Pt = 12 under 30 bar $H_2$ pressure and a platinum concentration of 200 ppm in water within 5 min reaction time in aqueous/organic two-phase systems (Table 2, entries 2/1–2/8). The formation of *trans*-C18:1 ester compounds increases with increasing temperature from 50 °C up to 120 °C to give from 0.4 up to 5.7 mol% *trans*-C18:1 esters (entries 2/1–2/8). At the higher temperature of 120 °C the selectivity towards *trans*-C18:1 stereoisomers remained low (5.7 mol%) which is even more remarkable when one considers that at 120 °C thermal *cis/trans*-isomerizations side reactions of unsaturated FAMEs take place to a considerable extent and that the MELO mixture was reduced to the level of IV = 89 while the Pt/TPPTS system exhibited a high catalytic activity of 6820 TOFs per hour (entry 2/8). This lower selectivity towards *trans*-C18:1 stereoisomer esters at the higher temperature of 120 °C could probably be rationalized by assuming that the Pt/TPPTS catalyst under these conditions may exhibited high catalytic activity in the hydrogenation reaction of *trans*-C18:1 esters to yield MS. In general, the *trans*-isomers are more difficult hydrogenated compared with their *cis*-counterparts. The different catalytic selectivity of Pt/TPPTS systems exhibited at the same reduction level of IV = 93 at reaction temperatures of 100 °C and 110 °C (Table 2, entry 2/6 and 2/7) regarding the formation of *trans*-C18:1 esters could be explained due the thermal *cis/trans*-isomerizations side reactions which yielded at 100 °C an amount of only 4.3 mol% *trans*-C18:1 esters (entry 2/6) whereas at the higher temperature of 110 °C the formation of *trans*-C18:1 esters was higher (5.0 mol%, entry 2/7).

### 3.1.4. Effect of hydrogen pressure and of the C=C units/Pt molar ratio

The effects of hydrogen partial pressure and of the molar ratio of C=C units/Pt in the biphasic partial hydrogenation of MELO is shown in Table 3. Both, the $H_2$ pressure and the C=C units/Pt molar ratio have a pronounced effect on the activity of the Pt/TPPTS cat-

alyst. The catalyst activity increased with increasing pressure and increasing molar ratio of the C=C units of MELO to the platinum catalytic complex. First, the effect of hydrogen pressure on the biphasic partial hydrogenation reaction of MELO was examined at a molar ratio of C=C units/Pt = 1000 (entries 3/1–3/4). The catalytic activity increased from TOF = 2350 $h^{-1}$ to TOF = 4250 $h^{-1}$ with increasing $H_2$ pressure from 20 to 50 bar at a reaction temperature of 60 °C and molar ratios of C=C units/Pt = 1000, TPPTS/Pt = 12, a platinum concentration of 200 ppm in water within 5 min reaction time in aqueous/organic two-phase systems (entries 3/1–3/4). The selectivity towards the total amount of the C18:1 ester isomers increases with increasing $H_2$ pressure to give under 20 bar a total content of 31.4 mol% and under 50 bar pressure 39.3 mol% of C18:1 compounds (entries 3/1–3/4). A small increase in the selectivity of the *trans*-C18:1 esters from 0.5 to 1.2 mol% was observed with increasing hydrogen partial pressure from 20 to 50 bar probably because *cis/trans*-isomerization reactions take place to a greater extent at higher hydrogen pressures (entries 3/1–3/4). As expected, the selectivity towards the undesired saturated product MS increased from 6.8 to 12.0 mol% with increasing pressure from 20 to 50 bar (entries 3/1–3/4). The catalytic activity increased from TOF = 2060 $h^{-1}$ to TOF = 3730 $h^{-1}$ and the selectivity towards the undesired *trans*-C18:1 esters decreased from 6.7 to 1.5 mol% with increasing molar ratios of C=C units/Pt from 1000 to 4000 at a reaction temperature of 80 °C and 30 bar hydrogen pressure in the partial hydrogenation of MELO in aqueous/organic two-phase systems (entry 3/5 − 3/8). The desired effect of suppressing the formation of *trans*-C18:1 esters with increasing C=C units/Pt molar ratios could probably be rationalized by assuming that at higher concentrations of unsaturated FAME in the reaction mixture the steric hindrance on C=C units coordinated on the platinum sphere increases which lowers the extent of the *cis/trans*-isomerization side reaction. The selectivity to MS considerably decreased with increasing C=C units/Rh molar ratios to give 35.4 mol% MS at C=C units/Rh = 1000 (entry 3/5) and only 6.7 mol% MS with C=C units/Rh = 4000 (entry 3/8).

### 3.1.5. Effect of the nature of the transition metal modified with TPPTS and of heterogeneous Pt/Al₂O₃ system on the formation of trans-C18:1 esters

Table 4 presents the catalytic activity and selectivity of water-soluble palladium, rhodium and platinum TPPTS complexes in the hydrogenation reaction of MELO at molar ratios of TPPTS/Metal = 5 and of C=C units/Metal = 1000, a reaction temperature of 110 °C, 30 bar H₂ pressure within 60 min of reaction time in aqueous/organic two-phase systems. In the range of 55–70 IVs for the hydrogenated products the Pt/TPPTS catalytic complex gave the least amount of *trans*-C18:1 esters (10.3 mol%), followed by Rh/TPPTS (28.2 mol%), and then by Pd/TPPTS (33.5 mol%). Interestingly, with Pt/TPPTS catalytic complexes the formation of the saturated product MS was very low (2.93 mol%) compared with Pd/TPPTS and Rh/TPPTS complexes which were 25.3 and 39.3 mol% MS, respectively. However, the Pd/TPPTS catalyst provided a higher selectivity of 70.6 mol% towards the total C18:1 esters compared with Pt/TPPTS and Rh/TPPTS which were 59.6 and 57.4 mol%, respectively. Rh/TPPTS complexes exhibited the highest catalytic activity (TOF = 750 h⁻¹) followed by Pd/TPPTS (TOF = 740 h⁻¹) and then by Pt/TPPTS systems (TOF = 670 h⁻¹).

In order to elucidate the predominant of Pt/TPPTS catalyst a comparison experiment of the partial hydrogenation of MELO was carried out over a heterogeneous Pt/Al₂O₃ (5 wt.%) catalyst under the same reaction conditions namely at a molar ratio of C=C units/Pt = 1000, a reaction temperature of 110 °C, 30 bar H₂ pressure and reduction level of IV = 72 in aqueous/organic two-phase systems (Table 4, entry 4/4). With heterogeneous Pt/Al₂O₃ (5 wt.%) catalysts the formation of *trans*-C18:1 esters was low (10.5 mol%) almost in the same level produced by Pt/TPPTS catalysts (10.3 mol%). In sharp contrast, over heterogeneous Pt/Al₂O₃ catalysts the formation of the undesired saturated product was high (37.7 mol%) compared with the very low formation of MS (2.93 mol%) in the presence of water-soluble Pt/TPPTS catalysts. However, the catalytic activity of heterogeneous Pt/Al₂O₃ catalyst was very high (TOF = 2200 h⁻¹) compared with the lower activity (TOF = 670 h⁻¹) of the Pt/TPPTS systems. It should also be mentioned that in the hydrogenation reaction of MELO over heterogeneous Pt/Al₂O₃ catalyst even at a reduction level of IV = 72 a sufficient amount of C18:3 esters (2.9 mol%) still remained unreacted (entry 4/4) whereas with Pt/TPPTS at IV = 70 the conversion of C18:3 esters was quantitative (entry 4/3). It is well-known that industrially applied commercial heterogeneous Ni catalyst in the hydrogenation of soybean oil would not completely remove C18:3 esters at the reduction level of IV = 110 needed for optimal quality of the liquid salad oil product and also with industrially used heterogeneous copper chromite catalysts in the same hydrogenation reaction a sufficient amount of C18:3 esters (3.0–3.5 mol%) remained unreacted leading to lower oxidation stability and unacceptable odors of the product [8]. In the field of aqueous-phase molecular catalysis low reactivity of C18:1 fatty acid methyl esters to the saturated C18:0 ester, compared to the hydrogenation of polyunsaturated C18:3 and C18:2 counterparts is well-known. For example, Vigh et al. [94] have extensively used water-soluble Ru/TPPMS molecular catalysts [TPPMS = monosulfonated triphenylphosphine, P(C₆H₅)₂(C₆H₄-*m*-SO₃Na)] for hydrogenation of polar lipids in aqueous systems and found that polyunsaturated fatty acids were ended up in form of C18:1 acids which could only difficult be hydrogenated into their saturated C18:0 counterparts.

### 3.1.6. On the nature of water-soluble platinum TPPTS catalysts in the hydrogenation of MELO, mercury poisoning, effect of agitation speed and recycling experiments

The Pt/TPPTS catalyst used in this work was prepared *in situ* after complexation under argon of PtCl₂ with TPPTS in H₂O and subjection of the mixture to a hydrogen atmosphere under the chosen hydrogenation reaction conditions. Although the catalyst is added as a platinum(II) salt the actual catalyst is probably a platinum(0) TPPTS complex, *i.e.* Pt(TPPTS)₃ [52] formed *in situ* after complexation of PtCl₂ with TPPTS to give the platinum (II) complex *cis*-PtCl₂(TPPTS)₂ [48] which is further reduced under hydrogenation conditions to the actual catalyst Pt(TPPTS)₃ complex in aqueous media. It should be mentioned that a general comparison regarding the stability of the Pt(TPPTS)₃ catalyst with its analogous water-soluble Pd(TPPTS)₃ complex [39,40,68–75] in catalytic reactions in aqueous media shows that the Pt(TPPTS)₃ catalyst possesses a lower stability compared with the Pd(TPPTS)₃ catalytic system and that the Pt(TPPTS)₃ catalyst decomposes even at the low temperature of 60 °C much easier to metallic platinum especially at low TPPTS/Pt molar ratios.

The absence of an induction period in the MELO biphasic hydrogenation might suggest for a homogeneous nature of the catalyst and not to the presence of platinum catalytic nanoparticles [76].

In order to verify whether the MELO biphasic hydrogenation reaction proceeds homogeneously by Pt/TPPTS catalytic complexes in water we tested this catalyst by means of mercury poisoning experiments. Mercury is a well-known heterogeneous catalyst poison because of its adsorption onto the surface of transition metal(0) catalysts or due to amalgam formation and it is probably most effective in poisoning metals that form an amalgam like the platinum(0) metal [76–79]. A large excess of Hg(0) which is 300 equiv. over the Pt/TPPTS catalyst was added to the aqueous catalyst solution and the biphasic MELO hydrogenation reaction was performed according to the conditions described in entry 5/4 of Table 5. The addition of mercury(0) to the biphasic hydrogenation reaction mixture (Table 5, entry 5/4) results in significantly reduced TOF's of only 140 per hour compared with the catalytic activity of 1600 TOF's per hour obtained in the absence of Hg(0) under the same reaction conditions (Table 5, entry 5/3) which suggests that mercury has inactivated the catalyst. This result provides a good evidence of the presence of heterogeneous platinum(0) catalytic nanoparticles.

Transition metal(0) catalytic nanoparticles [83,84] stabilized with nitrogen- and phosphorous-containing ligands [85–87] have been applied in a broad spectrum of catalytic reactions. According to Roucoux [80,81,83,88] "…*stabilization of finely dispersed metallic particles in neat water by hydrosoluble protective agents is an original catalytic approach to prevent aggregation and to facilitate recycling…*" and stabilized water-dispersible transition metal(0) catalytic nanoparticles have been applied in several catalytic reactions in aqueous media [83,89]. Bayer and Schumann [90] applied water-dispersible palladium(0), platinum(0) and ruthenium(0) nanoparticle catalysts stabilized with poly(vinylpyrrolidone) (PVP) in hydrogenation reactions of alkenes, alkynes and arenes in aqueous/organic two-phase systems. The PVP-stabilized Pd nanoparticle catalyst was very effective in selective partial hydrogenation of soybean oil with negligible formation of both *trans*-stereoisomers and of stearic acid. The group of Monflier [91] developed novel aqueous-phase rhodium(0) nanoparticle catalysts stabilized with cyclodextrin-based polycarboxylates which exhibited high catalytic activities under mild reaction conditions in the partial hydrogenation of methyl linoleate in aqueous/organic two-phase system which allowed efficient recycling of the catalyst in four consecutive runs. Our group [75] developed water-dispersible palladium(0) nanoparticle catalysts stabilized by water-soluble nitrogen-containing ligands such as bathophenanthrolinedisulfonic acid disodium salt (BPhDS) which exhibited exceptionally high catalytic activities (TOF = 110,000 h⁻¹) in the partial hydrogenation of polyunsaturated methyl esters of soybean oil into their monounsaturated counterparts in aqueous/organic micellar systems. A recycling experiment at 120 °C showed that the activity of palladium(0) nanoparticle catalyst stabilized by BPhDS in micellar

systems in aqueous media remained high in a consecutive run indicating a stable palladium(0) catalytic nanoparticle system which is remarkable when one considers that transition metal(0) catalytic nanoparticles are usually applied at much lower temperatures due to their lower stabilities.

Table 6 presents the rate of the biphasic hydrogenation reaction of MELO catalyzed by platinum(0) nanoparticles as a function of stirring rate at 80 °C. In the range of 500–900 rpm the reaction rate was independent (TOF's almost unchanged between 1500 and $1600 \, h^{-1}$) of the stirring rate ensuring that mass transfer was not rate determining. These results obtained by water-dispersible platinum(0) nanoparticle catalysts stabilized by water-soluble TPPTS ligands in aqueous/organic two-phase systems were rationalized by assuming that the zwitterionic phospholipid surfactant lecithin inherent in the renewable MELO starting material creates micelles and thus lowers the mass transfer barrier making in such micellar catalytic reactors mass transfer not rate determining. This stabilization mechanism of the catalytic active platinum(0) nanoparticle (PtNP) is coordinative stabilization by phosphine ligands in the highly polar aqueous solvent and the catalytic hydrogenation activity and selectivity of MELO is enormously increased due to the presence of micellar nanoreactors as proposed in Fig. 1. Caporali et al. [92] reported water-dispersible palladium(0) catalytic nanoparticles to be stabilized by a known water-soluble phosphine ligand namely 1,3,5-triaza-7-phosphaadamantane and applied as catalysts in hydrogenation reactions in aqueous/organic two-phase systems. Moreover, the zwitterionic surfactant lecithin probably contributes with electrosteric stabilization and furthermore aqueous solvent molecules stabilize the PtNP catalytic system. There are four widely accepted stabilization mechanisms of transition metal(0) catalytic nanoparticles which were first introduced by Roucoux, Schulz and Patin [83] and include electrostatic, steric, electrosteric and coordinative stabilization by a ligand or a solvent [89]. The micelle core of Fig. 1 is composed of the hydrophobic chain of the zwitterionic phospholipid surfactant lecithin where the hydrophobic tail of ML with the C=C unsaturation units are located. Surrounding the core is the Stern layer where the charged head groups $NMe_3^+$ and $SO_3^-$ of the phospholipid surfactant lecithin and TPPTS, respectively, are located together with the polar ester group of ML along with the counter ions ($Cl^-$ and $Na^+$) of the ionic micelle. The PtNP catalyst is probably located on the polarity gradient between the Stern layer and the micelle core. It should also be mentioned that the catalytic hydrogenation reaction may proceed in "wet micelles" which are water-permeated micelles and water molecules are present within the micelle core [39,93].

The apparent Arrhenius parameter of the activation energy of the Pt/TPPTS-catalyzed hydrogenation reaction of MELO in aqueous/organic two-phase systems was calculated from results obtained from biphasic hydrogenation reactions carried out at temperatures 50–120 °C and are summarized in Table 2, entries 2/1–2/8. The apparent activation energy which was calculated with these data (Fig. 2) amounts to 17.8 kJ/mol. The low apparent activation energy of 17.8 kJ/mol indicates for the presence of a very active platinum(0) TPPTS catalyst [82].

A recycling experiment with a consecutive run were carried out in the hydrogenation of MELO in order to get more information for the stability of Pt/TPPTS catalysts in aqueous/organic two-phase systems (Table 5, entries 5/1 and 5/2). 2.66 mg (0.01 mmol) $PtCl_2$ and 111.3 mg (0.18 mmol) TPPTS (TPPTS/Pt molar ratio = 18) were added to 10 ml of deaerated demineralized $H_2O$ and the mixture was stirred with slight heating for about 10 min to give a clear slightly yellow almost uncoloured solution. The aqueous solution of Pt/TPPTS catalyst was charged with 3.331 g (20 mmol of C=C units) of MELO 2 mixture into an *Autoclave Engineers* autoclave (100 ml) which was equipped with a stir bar driven by an IKA magnetic stirrer (poorer mixing) because its own MagneDrive III agitator

system was out of order (stirring rate = 700 rpm). In the reaction mixture the molar ratio of C=C units/Pt was 2000. After a number of pressurizing-depressurizing cycles with hydrogen to remove last traces of air oxygen, the autoclave was pressurized and contents were heated with stirring. The heating time to reach a reaction temperature of 80 °C was 2 min. At the reaction temperature of 80 °C the hydrogen partial pressure was 30 bar and the reaction time 30 min. After the reaction the autoclave was cooled (within 3 min) to room temperature, vented of hydrogen and the reaction mixture removed. After the reaction the Pt/TPPTS catalyst was easily recovered by a simple phase separation of the aqueous slightly yellow almost uncoloured phase from the upper organic yellow layer and the aqueous phase containing the catalyst after separation of a minor amount of metallic platinum was re-used under the same hydrogenation reaction conditions after addition of a new portion of 3.331 g (20 mmol of C=C units) of MELO 2 mixture. After the recycling hydrogenation experiment a minor amount of metallic platinum formation was observed and the pH value of the aqueous catalyst solution was 3.51. The catalytic activity remained relatively high (TOF = $1400 \, h^{-1}$) using the recycled Pt/TPPTS catalyst in the biphasic hydrogenation experiment of entry 5/2 compared with the first biphasic reaction of entry 5/1 using the Pt/TPPTS catalyst (TOF = $1700 \, h^{-1}$). It should be mentioned that at higher TPPTS/Pt molar ratios than 18 this catalytic system is more stable under hydrogenation reaction conditions with no metallic platinum formation and may possess the potential to be recycled without any loss of catalytic activity. This recycling experiment of the partial hydrogenation of MELO at 80 °C catalyzed by heterogeneous platinum (0) nanoparticle catalyst stabilized by TPPTS in micellar systems in aqueous media with a small loss of activity in a consecutive run also at 80 °C indicates a relative stable platinum(0) catalytic nanoparticle system which is remarkable when one considers that transition metal(0) catalytic nanoparticles are usually applied at lower temperatures due to usually their lower stabilities.

## 4. Conclusions

The work presented in this paper demonstrated again the high potential of green and sustainable aqueous-phase catalysis through a new application. We have shown that in the presence of water-dispersible platinum(0) nanoparticle catalysts stabilized by TPPTS ligands and the zwitterionic phospholipid surfactant lecithin the partial hydrogenation reaction of polyunsaturated methyl esters of linseed oil (MELO) into their monounsaturated counterparts proceeds smoothly under mild reaction conditions (T = 50–120 °C and $P_{H2}$ = 20–50 bar) with high catalytic activities (TOF = $6820 \, h^{-1}$) and very low formation of both undesired products namely *trans*-C18:1 esters (0.1 mol%) and the fully hydrogenated methyl stearate (4.6 mol%) in aqueous/organic two-phase micellar reactors. The reaction rate was independent of the stirring rate ensuring that mass transfer was not rate determining. The apparent activation energy of the Pt/TPPTS catalyst was calculated and amounts a low value of 17.8 kJ/mol. Employing Pt/TPPTS catalysts the starting material MELO possessing an iodine value (IV) of 202 was reduced to IV = 85 and contained only 2.4 mol% of *trans*-C18:1 esters. In contrast, in the traditional industrial partial hydrogenation process of soybean oil possessing an IV of 130 reduced over commercial Ni-based catalyst to IV = 80 the *trans*-fats content was ~30 mol% whereas with a further reduction to IV = 70 to produce all-purpose shortenings the *trans*-fats level reached a higher value of ~45 mol%. In the aqueous-phase catalysis, in the range of 55–70 IVs for the hydrogenated products of MELO the Pt/TPPTS catalysts gave the least amount of *trans*-C18:1 esters followed by Rh/TPPTS and then by Pd/TPPTS complexes. Interestingly, with Pt/TPPTS catalysts the formation of MS was very
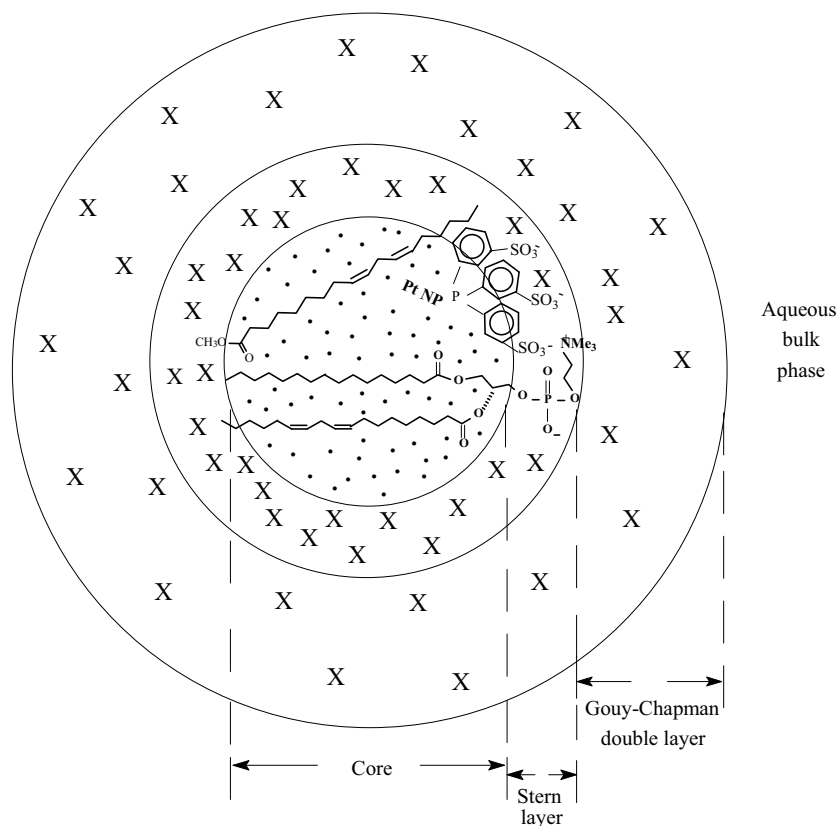
**Fig. 1.** Representation of a simplified proposed model of a spherical Hartley ionic micelle containing the platinum(0) nanoparticle (PtNP) catalyst stabilized by a TPPTS ligand, the zwitterionic phospholipid surfactant lecithin (phosphatidylcholine) and the starting material ML. The hydrophobic tails of lecithin and of ML in the core of the micelle (stippled part), the hydrophilic heads ($NMe_3^+$) interacted with the $SO_3^-$ groups of the TPPTS ligand stabilizer in the Stern layer, the hydrophilic groups of ML in the Stern layer and Gouy-Chapman double layer, the counter ions (Na$^+$ and Cl$^-$ depicted as X) schematically indicate their relative locations and not the relationship to their molecular size, distribution, number or configuration.
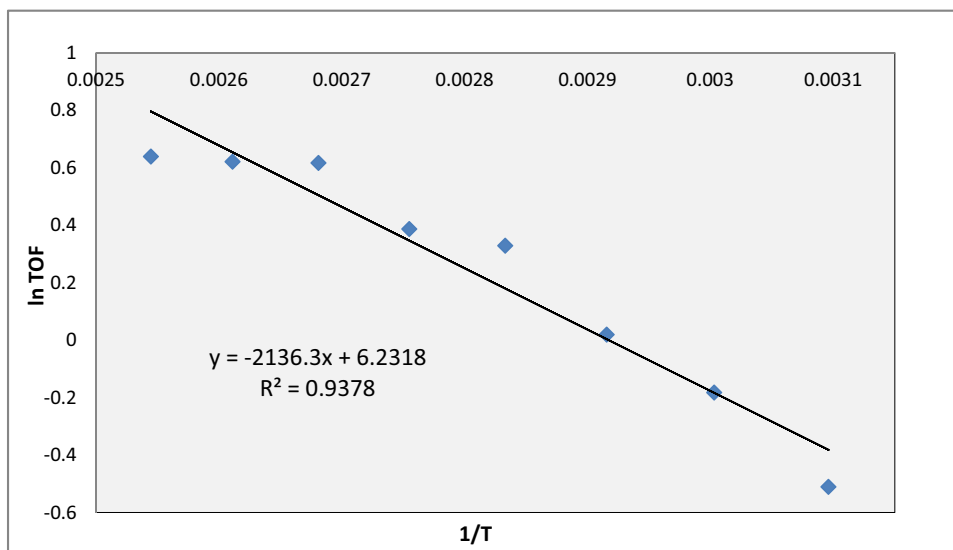


**Fig. 2.** Calculation of the apparent Arrhenius parameter of the activation energy of the hydrogenation reaction of MELO catalyzed by water-dispersible platinum(0) nanoparticle catalysts stabilized by water-soluble TPPTS ligands in aqueous/organic micellar systems.

low compared with Pd/TPPTS and Rh/TPPTS systems. Over highly active heterogeneous Pt/Al$_2$O$_3$ (5 wt.%) catalysts the formation of *trans*-C18:1 esters was low whereas the content of MS was high (37.7 mol%) compared with the very low formation of MS (2.93 mol%) with Pt/TPPTS catalysts. Even at a reduction level of IV = 72 a sufficient amount of C18:3 esters (2.9 mol%) still remained

over Pt/Al$_2$O$_3$ catalysts whereas with Pt/TPPTS at IV = 70 the conversion of C18:3 esters was quantitative. A recycling experiment at a higher temperature of 80 °C showed that the catalytic activity of water-dispersible platinum(0) nanoparticle catalysts stabilized by TPPTS remained high in a consecutive run and possess the potential to be recycled without any loss of catalytic activity.

Hence, we are currently investigating the scope of this useful partial hydrogenation reaction of MELO employing platinum(0) nanoparticle-TPPTS-lecithin-stabilized catalytic systems for studying the selective partial hydrogenation of edible vegetable oils to foodstuffs with very low or zero amounts of both undesired *trans*-fats and fully saturated fats employing environmentally attractive aqueous/organic two-phase systems.

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